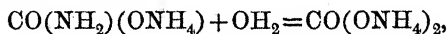


III. "On the Limited Hydration of Ammonium Carbamate."

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It occurred to me that a study of the action of water on ammonium carbamate, with reference to the influence of time, mass, and temperature, would be of interest as tending to throw light upon the laws which govern a chemical action of the simplest type in the liquid state—the action consisting of the direct union of two simpler molecules to form one more complex—

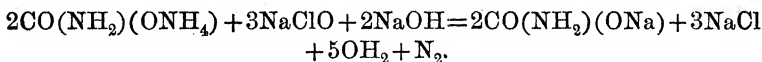


There are but few such actions which can be investigated, where all the substances are in the liquid state and all extraneous matter absent.

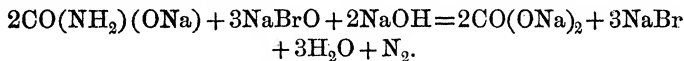
In a paper read before the Chemical Society in 1879,* I showed that ammonium carbamate when acted upon by sodium hypochlorite in

* "Chem. Soc. Jour.," 35, 12.

presence of sodium hydroxide, yields one-half of its nitrogen in the free state, the other half remaining in the form of sodium carbamate—



Sodium hypobromite at once decomposes sodium carbamate, evolving its nitrogen in the free state—



This, in fact, may be claimed as a specific reaction for carbamates—no other substance yet investigated will yield nitrogen when treated with a hypobromite *after* the completed action of a hypochlorite. Urea evolves but half its nitrogen with a hypochlorite, in presence of caustic alkali, but the other half remains as a cyanate, which is not acted upon by a hypobromite.*

Based upon this reaction, then, we have a direct and simple method of determining the amount of carbamate existing in a solution at any given time.

Since, under the action of a hypochlorite, ammonium carbamate yields one-half of its nitrogen (*i.e.*, that present as ammonium), it is evident that any excess over and above this half which is evolved from its solution, is a measure of the water which has been assimilated converting the carbamate into carbonate.

For the sake of convenience we may express the hydration which occurs in terms of the ratio of the number of molecules of water assimilated to that of the molecules of ammonium carbamate taken. Let V = the total volume of nitrogen contained in the ammonium carbamate taken, and V_1 = that evolved by the action of a hypochlorite on its solution. Then the above ratio evidently = $\frac{2V_1 - V}{V}$ (since one atom of nitrogen evolved in excess of the half total corresponds to one molecule of water assimilated, and two atoms of nitrogen originally present represent one molecule of ammonium carbamate taken).

The ammonium carbamate used in these experiments was prepared by the direct union of carefully dried ammonia and carbon dioxide. The apparatus employed in the estimation of the evolved nitrogen was similar to that described in a former paper on the action of Hypochlorites in Urea.*

Experiments were undertaken with a view of investigating to what extent the action is influenced by (1) time, (2) mass, (3) temperature, and (4) to study the reverse action, namely, the dehydration of normal ammonium carbonate into ammonium carbamate.

* "Chem. Soc. Jour.," 33, 300.

I. *Influence of Time.*

Weighed quantities of ammonium carbamate were dissolved in water and the solutions made up to a definite volume. Measured portions were then withdrawn and examined at stated intervals by treatment with sodium hypochlorite and sodium hydroxide, care being taken to employ approximately the same quantities of reagents for each experiment of the series. The times were reckoned from the moments of complete solution of the salt.

6.2873 grams ammonium carbamate were dissolved in water—the solution made up to 100 c.c. and 5 c.c. (corresponding to 0.31437 gram of carbamate) taken for each experiment. Theory for total nitrogen = 90.20 c.c.

Minutes.	Intervals.	c.c. of Nitrogen (corrected).	Hydration.
5	1	54.16	0.2008
10	2	56.71	0.2575
20	4	60.37	0.3386
40	8	66.04	0.4644
60	12	68.60	0.5211
100	20	71.44	0.5842
120	24	72.08	0.5983
160	32	72.72	0.6125

After a further interval of about 24 hours, 72.28 c.c. of nitrogen were evolved. Similar experiments were made with a weaker solution, namely, one containing 4.8781 grams of ammonium carbamate in 250 c.c.; 10 c.c. were taken for each determination, corresponding to 0.1951 gram of carbamate, and to a total of 55.98 c.c. of nitrogen.

Minutes.	Intervals.	c.c. of Nitrogen (corrected).	Hydration.
5	1	35.09	0.2536
10	2	38.72	0.3833
20	4	40.91	0.4615
40	8	43.20	0.5434
60	12	45.70	0.6327
120	24	47.47	0.6960
220	44	47.57	0.6995

After about 24 hours 47.96 c.c. of nitrogen were obtained.

It is evident from these results that the action, which proceeds rapidly at first, becomes progressively slower, and finally reaches a limit short of complete hydration.

The time required to reach a determinate state of hydration is evidently greater for a strong solution than a weak one, *i.e.*, decreases as the relative number of water molecules increases.

II. *Influence of Mass.*

8.3272 grams of ammonium carbamate were dissolved in water and the solution made up to 100 c.c. (Solution A.)

25 c.c. of solution A were made up to 50 c.c. (Solution B.)

25 c.c. of solution A were made up to 250 c.c. (Solution C.)

The relative strengths were therefore $A : B : C :: 1 : \frac{1}{2} : \frac{1}{10}$.

The solutions were set aside for four days in carefully stoppered flasks and under similar conditions. Volumes of each solution which corresponded to equal masses of ammonium carbamate were then withdrawn—namely, 5 c.c. of A, 10 c.c. of B, and 50 c.c. of C, representing 0.41636 gram of carbamate—and examined by the hypochlorite method in the usual way.

5 c.c. of A gave 95.73 c.c. N (corr.).

10 " B " 99.99 "

50 " C " 110.60 "

In order to be certain that the equilibrium state had been arrived at, the same solutions were again examined after a further interval of two days, when

5 c.c. of A gave 95.35 c.c. N (corr.).

10 " B " 99.96 "

50 " C " 110.83 "

showing that the limits had been reached in the former experiments. These numbers correspond to the hydrations—

A 0.5963

B 0.6735

C 0.8550

In order further to confirm these results, the residues from the last experiments, after the completed action of the hypochlorite, were treated with sodium hypobromite in order to estimate the nitrogen remaining as carbamate.

Residue from A gave 22.02 c.c. N (corr.).

" " B " 17.50 "

" " C " 8.01 "

making the totals—

A 117.37 c.c. N (corr.).

B 117.46 "

C 118.84 "

theory for 0.41636 gram ammonium carbamate requiring 119.46 c.c. There is always a loss of about 8 per cent. of nitrogen in estimations

with hypobromite*: if this correction be applied the agreement will be still closer.

In order to facilitate the interpretation of the results, further experiments were made in the same direction, using mixtures of carbamate and water in simple ratios of their molecular weights.

					Mols. of carbamate.	Mols. of water.
(a)	0·3270	gram am. carb.	with 15·09	grams water,	corresponding to	1 : 200
(b)	0·1836	"	"	12·71	"	1 : 300
(c)	0·1307	"	"	12·06	"	1 : 400
(d)	0·1042	"	"	12·02	"	1 : 500

After standing for some days under similar conditions the following results were obtained :—

		c.c. of N (corr.) obtained.		Theory for total nitrogen.		Hydration.
(a)	82·02	93·80	0·7487
(b)	47·29	52·66	0·7962
(c)	34·57	37·49	0·8447
(d)	28·62	29·89	0·9156

Another experiment was made in which the ratio of the molecular weights was nearly 1 : 1, namely, 0·2614 gram ammonium carbamate with 0·0632 gram water. After standing for two days, 49·52 c.c. nitrogen (corr.) were obtained—theory for total nitrogen requiring 75·0 c.c. The hydration was therefore 0·3187.

It follows from the above results that the hydration is a function of the number of water molecules present. So far the minimum hydration corresponds to the case in which the substances are present in about equal molecular proportions, and is in this respect analogous to the combination of iodine with hydrogen† and of phosphorus trichloride with chlorine.‡ From analogy it was to be expected that the hydration would again increase as the ratio of the ammonium carbamate molecules to those of water increased; but the experiment cannot be made under the same conditions as those above, since with any appreciable excess of the carbamate the water is insufficient to completely moisten the solid.

III. Influence of Temperature.

The above results may be taken as representing the phenomena which occur at about 20—22° C., from which the temperature varied but little throughout the experiments.

* Russell and West, "Chem. Soc. Jour.," 27, 749.

† Lemoine: "Équilibres Chimiques entre l'Hydrogène et l'Iode Gazeaux," Ann. Chem. Phys." [5], xii, 145.

‡ Wurtz, "Comptes Rendus," lxxvi, 602.

In order to gain some idea as to the effect which temperature might have upon the action, two equal volumes of an arbitrary solution of ammonium carbamate were taken and kept in sealed vessels, one at the temperature of the room—about 15°C ., and the other in melting ice. After about five hours the solutions were examined by the hypochlorite method, taking care to keep the apparatus in each case as nearly as possible at the respective temperatures.

Solution at 0°C . gave 68.0 c.c. N (corr.).

„ 15 „ 79.4 „

Similar pairs of experiments were made with another solution at stated intervals, equal volumes being measured out in the first instance and then subjected to the respective temperatures in sealed vessels.

After 30 minutes solution at 0° gave 63.7 c.c., solution at 15° gave 76.2

„ 1 hour „ „ 73.0 „ „ 83.2

„ 2 hours „ „ 74.0 „ „ 88.9

„ 4 „ „ „ 76.3 „ „ 90.6

The hydration is therefore, in all cases, less at the lower temperature.

The minimum hydration will probably occur at a sufficiently low temperature, and when the substances are present in equal molecular proportions. A mixture was made of 0.6199 gram ammonium carbamate with 0.1424 gram of water—corresponding almost exactly to equal molecular weights. This mixture was kept in a sealed tube placed in a block of ice for 18 hours, when it may be safely assumed that the equilibrium state was arrived at. It was then examined by the hypochlorite method (the apparatus being kept at about 0°C . throughout), and yielded 95.90 c.c. of nitrogen (corrected). Theory for total nitrogen requires 177.1 c.c., so that the hydration is represented by 0.0830.

Probably, at a sufficiently low temperature, the hydration would be practically *nil*, when the substances are present in molecular proportions—*i.e.*, ammonium carbamate and water would practically *not combine at all*—resembling the cases of phosphorus trichloride and chlorine, &c., at sufficiently *high* temperatures.

IV. *Dehydration of Normal Ammonium Carbonate.*

The salt was prepared by the method of Divers.* About 5—6 grams of it were dissolved in water, and the solution made up to 100 c.c. (A). Portions of this solution were diluted to $\frac{1}{2}$ (B) and $\frac{1}{10}$ (C). After two days—

* “Chem. Soc. Jour.,” 23, 179.

5 c.c. of A	gave	35·54 c.c. N (corr.)	
10 „ B	„	38·10	„
50 „ C	„	40·85	„

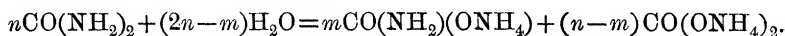
Equal volumes of another solution were examined at intervals, with the following results:—

After 5 minutes	67·94 c.c. N (corr.)	were evolved.
„ 40 „	66·73	„ „
„ about 3 hours	62·52	„ „
„ „ 24 „	62·28	„ „

These results indicate that normal ammonium carbonate undergoes dehydration into carbamate when in solution, and that the dehydration is greater as the relative number of water molecules is less.

The instability of normal ammonium carbonate, and the difficulty of obtaining it free from adhering impurities has, for the present, prevented me from making more extended observations on this part of the subject. It seems not unlikely, that if the same relative number of molecules could be started with, the same equilibrium state between carbamate, carbonate, and water, would be arrived at for the same temperature, whether ammonium carbamate or normal carbonate were initially taken—that is, that the curves of hydration and dehydration would meet at the same point. I hope before long to be able to make experiments in this direction.

Since there is this tendency for ammonium carbonate to become in part dehydrated in aqueous solution, and for the system to come to a state of equilibrium where the carbamate and carbonate co-exist, it seems probable that the hydrolysis of urea, under the action of ferments, &c., may be less simple than is usually represented—that the reaction, instead of being simply $\text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O} = \text{CO}(\text{ONH}_4)_2$, may be of the following type:—



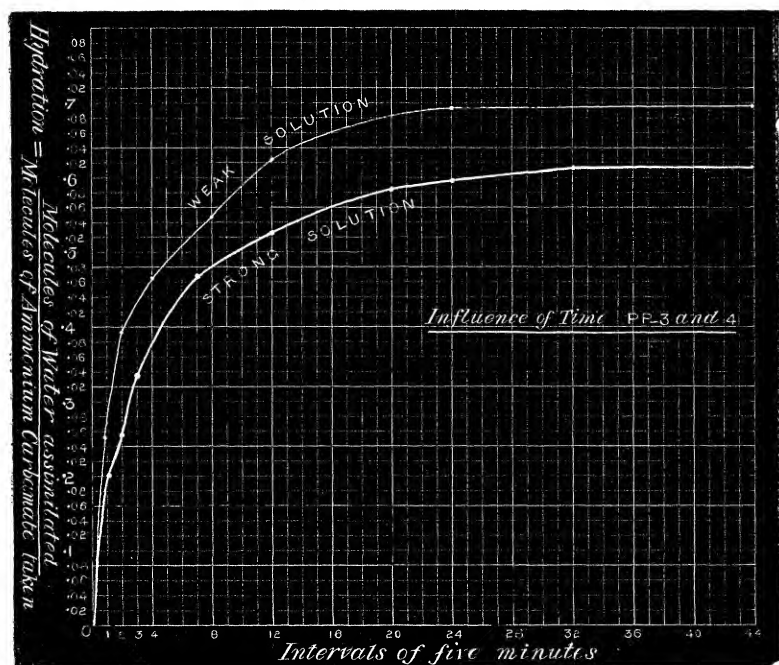
I propose to attack this subject by the same method as those employed above.

By means of the actions of sodium hypochlorite and hypobromite it is evidently possible and easy to estimate quantitatively *urea*, *carbamie acid*, and *ammonia*, when all are present in the same solution.

Take two equal portions of the solution to be examined, treat one with sodium hypobromite, and let the volume of nitrogen evolved (corrected for loss) = V_1 .

Treat the other portion with sodium hypochlorite, and let V_2 = volume of nitrogen obtained.

Act upon the residue from this last experiment with sodium hypo-



bromite, and let V_3 represent the volume of nitrogen given off (corrected).

Let x = volume of nitrogen due to urea.

„ y = „ „ ammonia.

„ z = „ „ carbamic acid.

Then

$$(1.) \quad x + y + z = V_1.$$

$$(2.) \quad \frac{x}{2} + y = V_2.$$

$$(3.) \quad z = V_3.$$

A preliminary trial of this method with a mixture of urea and ammonium carbamate gave very satisfactory results.

It appears to me that no really satisfactory method has hitherto been known by which carbamic acid could be detected and estimated in presence of urea and ammonia, so that the process indicated above may perhaps be of service in investigations bearing on the formation of urea in the animal body, and its origin, whether carbamic or otherwise.

Hydration = $\frac{\text{Moles of water absorbed}}{\text{Moles of Anhydrous Calcium Oxide taken}}$

